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Structural ordering and dynamics of LaH_{3-x}

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Abstract

The structural arrangements, optic-vibrational density of states, and diffusive motions of hydrogen (and deuterium) in the light-rare-earth hydride LaH_{3-x} (for small hydrogen-vacancy fractions x) have been measured by neutron powder diffraction, neutron vibrational spectroscopy, and quasielastic neutron scattering. Diffraction measurements of LaD_{3-x} indicate preparation-dependent changes in structural ordering below room temperature. Vibrational spectra of both pure and isotopically mixed samples reflect the presence of significant H–H interactions involving the hydrogen located in the octahedral and tetrahedral interstices of the fcc metal sublattice. Quasielastic scattering measurements above room temperature reveal two types of hydrogen motions: a localized ‘rattling’ motion of the octahedrally coordinated hydrogen and a long-range diffusional motion via the hydrogen vacancies. A sample color change from black to copperish-orange observed in the vicinity of the highest hydrogen concentrations likely reflects a transition from optical opacity to optical transparency, as reported for LaH_{3-x} thin films. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Both the hcp and fcc rare-earth trihydrides have been the subject of much interest in recent years due to the discovery of their novel switchable optical properties [1]. It is clear that hydrogen plays a critical role in promoting optical transparency in these materials. Characterization of the structural arrangements, vibrational dynamics, and diffusive motions of hydrogen in the rare-earth trihydrides is important for gaining a better understanding of this phenomenon. Previously we have reported on the hydrogen structural arrangements of the hcp-based rare-earth trihydrides [2–4]. In this paper, we report on the progress of neutron-powder-diffraction (NPD), neutron-vibrational-spectroscopy (NVS), and quasielastic-neutron-scattering (QENS) studies of the structure and dynamics of fcc-based lanthanum trihydride (LaH_{3-x}) powder specimens.

2. Experimental details

Lanthanum trihydrides, trideuterides, and mixed isotope analogs were prepared by gas-phase absorption, similar to previous syntheses [3,5]. To minimize the problems associated with impurities, only high-purity (99.99 at.%) metals

and research grade H_2 and D_2 were used. Typically, 10–25 g metal ingot samples were evacuated in a quartz tube up to 873 K, followed by quantitative absorption of H_2 and/or D_2 gas and a subsequent overnight cool-down to room temperature. The resulting hydride (or deuteride) samples were pulverized in a He-filled glovebox, loaded into the appropriate flat-plate or cylindrical Al containers, and sealed with a Pb or In gasket.

All NPD, NVS, and QENS measurements were performed at the NIST Center for Neutron Research. For NPD measurements, the high-resolution, 32-counter BT-1 diffractometer was used with the Cu(311) monochromator at a wavelength of 1.5391(1) Å. For NVS measurements, the BT-4 spectrometer was used with the Cu(220) monochromator and 40′–20′ front-end collimations in conjunction with the high-resolution Be-graphite-Be filter analyzer. The instrumental resolution (full width at half maximum, FWHM) is indicated by horizontal bars beneath the vibrational spectra. For QENS measurements, the Fermi-Chopper Time-of-Flight Spectrometer was used at 4.8 Å incident wavelength providing a nominal elastic scattering resolution of 146 μeV FWHM.

3. Results and discussion

For hydrides of Y and the heavier rare-earth metals, there is a phase change from an fcc to hcp metal sublattice

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upon going from the dihydride to trihydride stoichiometry. As a result, a two-phase region typically exists for intermediate hydrogen concentrations. In contrast, for hydrides of the light-rare-earth metals such as La and Ce, an fcc metal sublattice is maintained over the entire range of hydrogen concentrations. Within this sublattice, hydrogen resides in the two tetrahedral (*t*) interstitial sites and one octahedral (*o*) interstitial site per metal atom. Any hydrogen interstitial vacancies are situated primarily within the *o*-site sublattice.

The maximum D/La stoichiometry ($x \sim 0.01$) obtained for LaD_{3-x} (under 0.56 MPa D_2) as calculated from profile refinements is in line with the low vacancy fractions determined from H_2 and D_2 uptake measurements. It is somewhat puzzling why there is such a discrepancy between the vacancy fractions found for our bulk powder materials and the order-of-magnitude higher values reported for polycrystalline LaH_{3-x} thin films [1], since both types of materials are synthesized under similar conditions of temperature and pressure. More work needs to be done to characterize the effects of substrate clamping and accompanying lattice strain on the structure and stoichiometry of thin-film specimens as compared with bulk materials.

Our preliminary structural data [6] on LaD_{3-x} ($x \sim 0.01$) indicated a phase transition upon lowering the temperature below ~ 260 K, as suggested by earlier measurements [7]. This was manifested by a redistribution of some Bragg-scattering intensity away from the main [220] peak into a series of closely spaced satellite lines. Subsequent X-ray-diffraction measurements [8] of this sample displayed an unexpectedly similar redistribution of Bragg-scattering intensity with temperature, indicating that a long-range-ordered pattern of displacements of the La metal atoms from the ideal fcc symmetry was occurring in addition to possible long-range-ordered displacements within the D sublattices. Preliminary analysis of the results suggests that the ordering may be incommensurate in nature. We are performing further temperature- and concentration-dependent investigations in order to develop a more complete understanding of the types of ordered La and D displacements (as well as ordered *o*-site vacancy arrangements) that would be consistent with the observed diffraction data.

Prior to measuring the NPD patterns, this particular sample was pulverized for only a short time before a final treatment in 0.31 MPa D_2 with cooling from 353 K to 295 K. The resulting material was black. Our more recent experiments have since ascertained that more extensive pulverization of the sample combined with higher treatment temperature and D_2 pressure causes significant changes to the temperature-dependent LaD_{3-x} structure. In particular, retreatment of the more finely pulverized sample in 0.56 MPa D_2 with cooling from 525 K to 295 K resulted in a copperish-orange material with a similar stoichiometry as the black precursor material as determined by profile refinement. This color change most likely

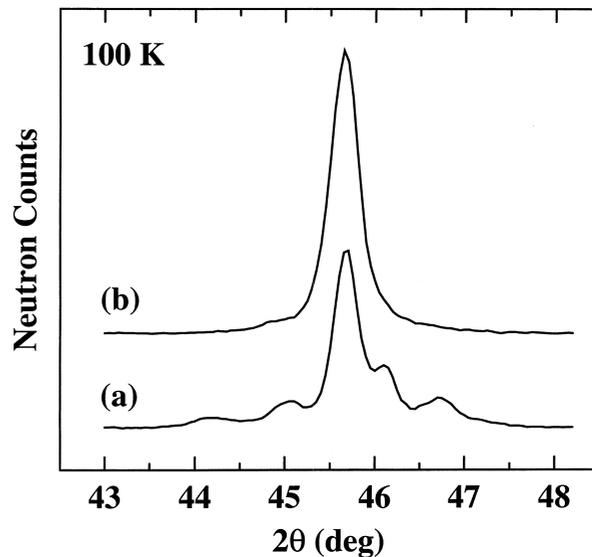


Fig. 1. The LaD_{3-x} diffraction pattern in the vicinity of the [220] reflection at 100 K for (a) the original 'black' sample and (b) the finely pulverized copperish-orange sample.

represents the transformation to the optically transparent phase of LaD_{3-x} . The resulting region around the [220] diffraction feature at 100 K is illustrated in Fig. 1 in comparison with the original 100-K pattern for the black LaD_{3-x} sample. It is clear that the satellite lines have largely disappeared, evidence that the low-temperature-ordering behavior has been impeded. This suggests that the additional sample treatment led to a phase change from an optically opaque material with ordered vacancies to an optically transparent material with disordered vacancies and a simple cubic structure possessing $Fm\bar{3}m$ symmetry. The nature of the vacancy arrangements is likely an important parameter behind the physics of optical switching in the light-rare-earth trihydrides [9].

From the measurements performed so far, it was postulated that a slight decrease in the vacancy fraction not easily observable by profile refinements was responsible for the apparent optical switching. Indeed, the difficulty in fully deuteriding LaD_{3-x} powder samples seems in line with the much slower kinetics found for fully hydriding 500-nm La films compared to the hydriding of similar Y films [1]. It is possible that submicron-sized particles of LaD_{3-x} are necessary for increasing the D/La ratio above the optical-switching transition under easily achievable temperatures and pressures. The diffraction measurements suggest that larger particles possess larger concentration gradients, leading to more inhomogeneous samples, which complicates interpretation of the resulting diffraction patterns.

To test our postulate concerning the effect of the vacancy fraction, we removed small amounts of D from the copperish-orange LaD_{3-x} sample to yield total changes of $\Delta x \approx -0.01$ and -0.03 and measured the 100-K diffraction pattern in each case. Surprisingly, neither of these

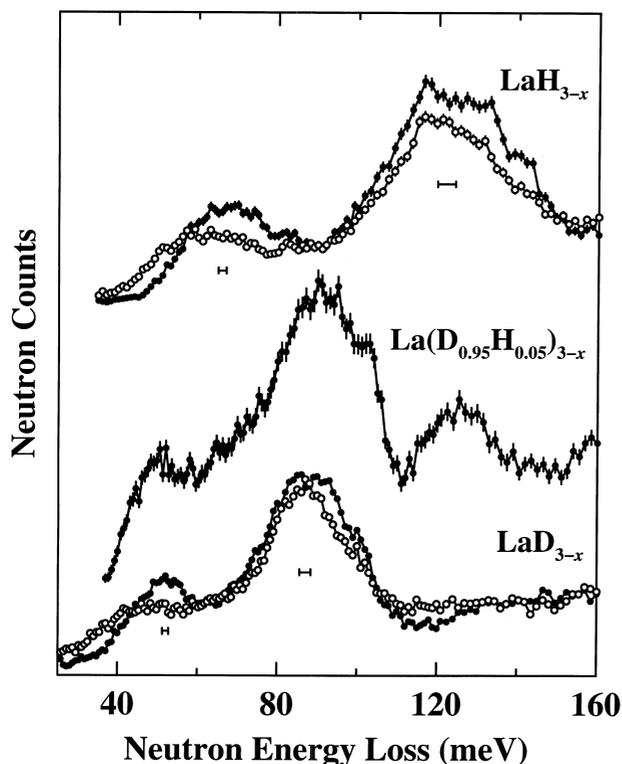


Fig. 2. The neutron vibrational spectra for LaD_{3-x} , $\text{La}(\text{D}_{0.95}\text{H}_{0.05})_{3-x}$, and LaH_{3-x} at 15 K (closed circles) and 300 K (open circles). The horizontal bars represent the FWHM instrumental resolution.

vacancy-enhanced samples led to the reemergence of the satellite lines reflective of the previous low-temperature ordered phase. Unfortunately for these experiments, the sample color was not monitored as a function of D removal. It is of particular interest to determine if the sample color and/or optical switching can be definitively correlated with the changes in the 100-K diffraction pattern. Hence, more experiments are currently being performed to determine the individual effects of particle size, temperature, and pressure on this puzzling region of the La–H phase diagram.

Fig. 2 illustrates neutron vibrational spectra measured for black LaD_{3-x} , $\text{La}(\text{D}_{0.95}\text{H}_{0.05})_{3-x}$, and LaH_{3-x} samples, which are considerably different than those for the hcp-based rare-earth trihydride systems [4,6]. At 15 K, the LaD_{3-x} spectra indicate two broad D optic-vibrational bands with roughly a 1:2 intensity ratio centered at ~ 52 and 87 meV, which are representative of D in the o and t sites, respectively. The corresponding energies shown in Fig. 3 for LaH_{3-x} are centered at ~ 66 and 122 meV. The broadening is a reflection of the phonon dispersion caused by significant D–D (H–H) interactions occurring in the concentrated deuteride (hydride), as well as the distribution of vibrational energies in the unusual low-temperature ordered structure caused by the displacements of La and D (H) from their ideal fcc positions. Upon isotope dilution of H with D in $\text{La}(\text{D}_{0.95}\text{H}_{0.05})_{3-x}$, there is an obvious narrowing and shifting of the high-energy H feature

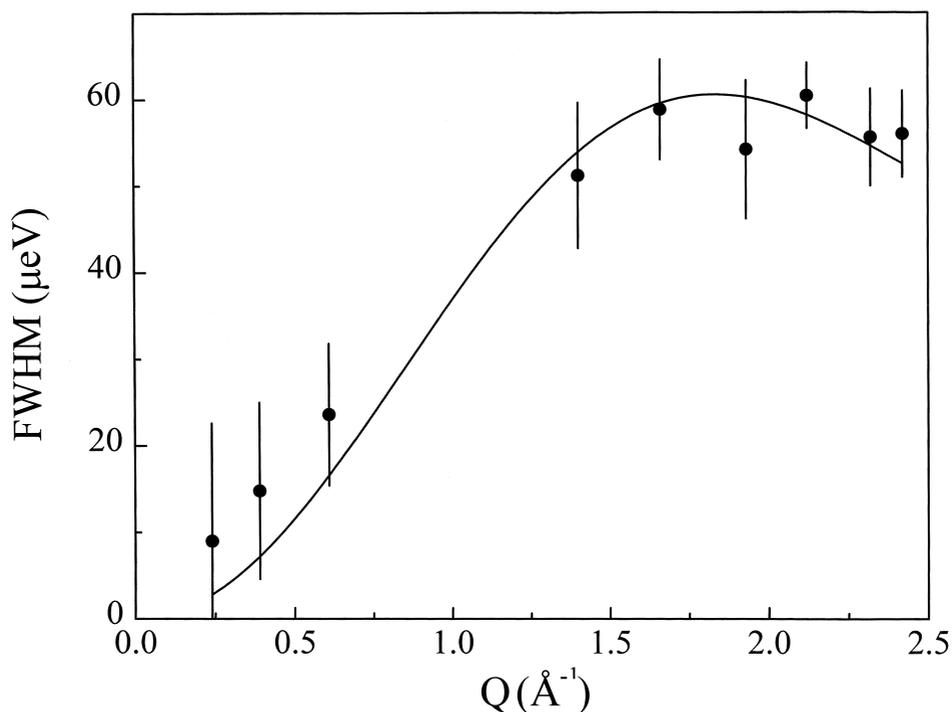


Fig. 3. The Q dependence of the narrow Lorentzian component peakwidth from the LaH_{3-x} QENS data at 540 K. The data are fit to an orientationally-averaged Chudley–Elliott model.

compared with LaH_{3-x} (the width of the low-energy H feature being partially masked by the D density of states), indicating a ‘turning off’ of H–H dynamic coupling interactions for the isotopically isolated H atoms, similar to what was observed in other isotopically diluted hydride systems [5,6,10]. Increasing the temperature to 300 K, which is above the ordering transition, leads to small but noticeable changes in the LaD_{3-x} vibrational bands compared to 15 K. The higher-energy band appears to have become slightly more gaussian suggesting that the *t*-site D atoms are now confined to their high-symmetry interstitial positions. The lower-energy band appears to have become slightly more broadened, although this is at least partly due to a multiphonon sideband contribution on the lower-energy side at this high temperature. Nonetheless, this could be an indication of increased disorder within the relatively large interstitial *o* site and/or the emergence of some line broadening due to a possible localized ‘rattling’ motion of the D atoms in these sites [11]. Indeed, there have been suggestions that the *o*-site D atoms prefer to be displaced along the [111] directions closer to three neighboring metal atoms rather than be situated exactly in the center of the relatively large *o* site [7].

We have corroborated such a motion in LaH_{3-x} by using QENS [12]. In particular, the QENS data above room temperature clearly indicate two Lorentzian quasielastic components with distinctively different FWHM peak-widths. From the momentum transfer (*Q*) dependences of the two components, the geometries of the underlying

motions were extracted. In particular, the narrower Lorentzian component was associated with long-range jump diffusion. As seen in Fig. 3, the corresponding FWHM at 540 K was in excellent agreement with an orientationally-averaged Chudley–Elliott model: $\text{FWHM} \propto (1 - \sin(Ql)/(Ql))$, where *l* is the jump distance. The preliminary data analysis revealed $l \approx 2.44 \text{ \AA}$, which is close to the distance between the *o* and *t* sites, strongly suggesting that the *x* *o*-site vacancies present in the substoichiometric trihydrides act as available sites for long-range hydrogen diffusion via *o*–*t* jumps. The temperature dependence of the narrow component yielded an activation energy of $150 \pm 10 \text{ meV}$ for the long-range diffusion. The broad Lorentzian component could be modeled with a nearly constant FWHM for all *Q* values at a given temperature. This was a strong indication that this component represented a localized hydrogen motion. The geometry of this motion could be derived from the *Q* dependence of the elastic incoherent structure factor (EISF), i.e., the ratio of the intensity of the narrow Lorentzian to the total quasielastic intensity, as exemplified at 540 K in Fig. 4. The line corresponds to an isotropic rotational motion on a sphere of 0.23 \AA radius for one-third of the hydrogen atoms (i.e. the *o*-site H atoms), although other related localized jump diffusion models such as jumps amongst the eight corners of a cube (which represents possible *o*-site H displacements away from the center position along the [111] directions) also fit the data. The small radius observed in the model fit is in line with the displacements expected for

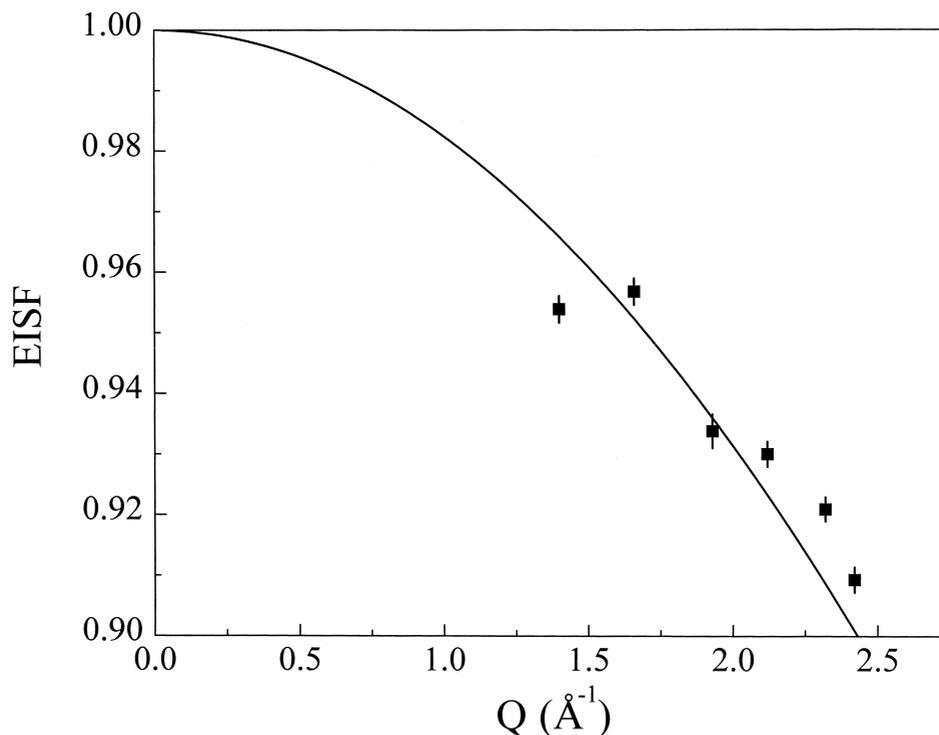


Fig. 4. The *Q* dependence of the EISF for LaH_{3-x} at 540 K. The data are fit with a model for isotropic rotational motion on a sphere for one-third of the H atoms.

the postulated ‘rattling’ motion of the *o*-site H atoms. The temperature dependence of the broad component yielded an activation energy of 73 ± 12 meV for the localized motion. The derived activation energies for both the long-range and localized hydrogen motions are in agreement with the values for hydrogen motions derived from solid-state NMR studies of LaH_{3-x} [13].

4. Summary

Both neutron-powder-diffraction and neutron-vibrational-spectroscopy studies have been undertaken to probe the structure and dynamics of fcc-based lanthanum-trihydride powder specimens. For LaD_{3-x} ($x \sim 0.01$), the previously observed low-temperature ordered phase largely disappears after additional sample pulverization and retreatment in D_2 (0.56 MPa) at higher temperature (525 K). The corresponding change in sample color from black to copperish-orange likely reflects a transition from optical opacity to optical transparency, as reported for LaH_{3-x} thin films. Additional structure and dynamics experiments are underway to characterize more thoroughly the nature of the ordered phase and its limited stability. Vibrational spectra of both pure and isotopically mixed samples reflect the presence of significant H–H interactions involving the hydrogen located in the octahedral and tetrahedral interstices of the fcc metal sublattice. Quasielastic scattering measurements above room temperature reveal two types of hydrogen motions: a localized ‘rattling’ motion of the

o-site hydrogen and a long-range diffusional motion via the *o*-site vacancies.

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